## **Supporting Information for**

## **Stereoisomeric Furan/Maleimide Adducts as Latent Monomers for One-shot Sequence-Controlled Polymerization**

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## **SECTION A. Experimental Section**

## 1. Monomer synthesis

1.1 Synthesis of endo-FMI



Scheme S1 Synthesis of monomer endo-FMI

Maleimide (9.7 g, 100 mmol, 1 eqv.) and furan (13.6 g, 200 mmol, 2 eqv.) were added to ultrapure water (400 mL) in an oven-dried 1.0 L three-necked round-bottom flask and the solution was stirred at room temperature for 5 days. The mixture was vacuum filtered and filter cake was washed with  $2\times50$  mL ultrapure water and then evaporated, a further purification was not necessary. Then dried to obtain the product (9.73 g, yield 59%) as a white powder. <sup>1</sup>H NMR (300 MHz, DMSO, ppm):  $\delta$  10.85 (s, 1H), 6.49 (s, 2H), 5.35 - 5.12 (m, 2H), 3.56 - 3.40 (m, 2H). <sup>13</sup>C NMR (75 MHz,

DMSO, ppm): δ 47.56, 78.99, 135.00, 176.96.



Fig. S1 (a) 300 MHz <sup>1</sup>H NMR spectrum in DMSO- $d_6$  of *endo*-FMI (b) <sup>13</sup>C NMR spectrum in DMSO- $d_6$  of *endo*-FMI



Fig. S2 High resolution mass spectrum of *endo*-FMI. High resolution mass spectrometer exact mass calculated for [M+Na]<sup>+</sup> C<sub>8</sub>H<sub>7</sub>NO<sub>3</sub> 165.0426, found 188.0316.

## 1.2 Synthesis of *exo*-FHMI



Scheme S2 Synthesis of monomer exo-FHMI

30.0 g maleic anhydride (305.9 mmol, 1 eqv) and 41.6 g furan (611.8 mmol, 2 eqv) were placed in a reaction flask equipped with the three-way stopcock, the mixture was dissolved into 300 mL anhydrous diethyl ether and stirred at room temperature for 36 h. After that the product precipitated out of solution and was collected via vacuum filtration, the filter cake was washed with 3×100 mL diethyl ether. The final product FMA was dried under vacuum at 30 °C overnight as a white solid (43.6 g, yield 85.9%).

10.0 g furan-protected maleic anhydride (FMA) (60.24 mmol, 1 eqv) and 40 mL methanol which served as solvent were added into a 100 mL three-neck flask equipped with a condenser. The three-neck flask was kept in an ice bath stabilized at -20 °C for 30 min. Then the mixture of 4.41 g ethanolamine (72.3 mmol, 1.2 eqv) and 10 ml methanol was cautiously added dropwise via a syringe into the three-neck flask. After complete addition, the reaction mixture was maintained at that temperature for 30 min more. The final mixture then was warmed up to room temperature and refluxed at 70 °C for 24 h. The solution was cooled to room temperature and stored in freezer one days. The product crystallized from the solution. Recrystallization from cool methanol and collected by vacuum filtered to give *exo*FHMI as a colorless transparent crystal. (5.97 g, yield 47.4%). <sup>1</sup>H NMR (300 MHz, DMSO, ppm)  $\delta$  6.55 (s, 2H), 5.12 (s, 2H), 4.78 (t, J = 4.8 Hz, 1H), 3.42 (d, J = 6.5 Hz, 4H), 2.92 (s, 2H). <sup>13</sup>C NMR (75 MHz, DMSO, ppm):  $\delta$  41.28, 47.82, 57.81, 80.74, 137.12, 176.95.





Fig. S3 (a) 300 MHz <sup>1</sup>H NMR spectrum in DMSO- $d_6$  of *exo*-FHMI (b) <sup>13</sup>C NMR spectrum in

## DMSO-d<sub>6</sub> of exo-FHMI



Fig. S4 High resolution mass spectrum of exo-FHMI. High resolution mass spectrometer exact mass

calculated for  $[M+Na]^+ C_{10}H_{11}NO_4 209.0688$ , found 232.0587.

## **1.3** Synthesis of PMI



Scheme S3 Synthesis of PMI

A typical procedure of synthesized MI was according to a literature protocol.<sup>1</sup> The crude product was purified by flash column chromatography on silica gel. Eluting with a mixed solvent of PE/EA (v/v = 8/1 to 4/1) as a clear and faint yellow oil. (10 g, yield 47.5%). <sup>1</sup>H NMR (300 MHz, DMSO, ppm)  $\delta$  7.10 - 6.92 (m, 2H), 3.36 (t, J = 13.2, 6.1 Hz, 2H), 1.61 - 1.37 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, DMSO, ppm):  $\delta$  11.46, 21.73, 40.262, 134.89, 171.70.





Fig. S5 (a) 300 MHz <sup>1</sup>H NMR spectrum in DMSO- $d_6$  of PMI (b) <sup>13</sup>C NMR spectrum in DMSO- $d_6$  of PMI

#### 2. Materials

Styrene (St, Sinopharm Chemical Reagent, 99%) was washed by 5% NaOH aqueous solution and deionized water for four times, dried by anhydrous MgSO<sub>4</sub> with a small amount of copper overnight and then distilled under vacuum. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to a literature protocol. 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN), 2,2-Azobisisobutyronitrile (AIBN) and 1,1'-Azobis (cyclohexanecarbonitrile) (ACHN) were purchased from Sinopharm Chemical Reagent, China (98%) and purified by recrystallization from ethanol.

Deuterated solvents were obtained from Deutero GmbH. Furan, maleimide, sodium sulfate anhydrous (99%), n-hexane (97%), methanol (99.7%), diethyl ether anhydrous (99.7%), dichloromethane (99.5%), ethyl acetate (99.5%), acetone were purchased from commercial supplier named Sinopharm Chemical Reagent Co.,Ltd. N, N-dimethylformamide (DMF, 99.9%) were purchased from Sigma-Aldrich. N-propylamine (99.7%) were purchased from Alfa Aesar. All reagents were used directly as received without further purification unless otherwise stated.

## 3. Analysis techniques

The number-average molecular weight ( $M_n$ ) and polydispersity ( $D = M_w/M_n$ ) of the polymers were determined using a size exclusion chromatograph (SEC) TOSOH HLC-8320 equipped with refractive index and UV detectors, using two TSKgel Super 20 Multipore HZ-N (4.6 × 150 mm, 3 µm bead size) columns arranged in a series with a molecular weight separation ranging from 500 to  $1.9 \times 10^5$  g/mol. DMF containing lithium bromide was used as the mobile phase (flow rate 0.7 mL/min at 40 °C). The dried crude copolymers were dissolved in DMF containing lithium bromide at 2 mg/mL concentration and filtered through a 0.45 µm PTFE syringe filter prior to inject. Data acquisition was performed using EcoSEC software, and molecular weights were calculated according to PS standards.

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of the samples were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) by using tetramethylsilane as the internal standard at room temperature. All spectra are referenced internally to residual proton signals of the deuterated solvent. The <sup>1</sup>H NMR spectra were referenced to  $\delta$  2.50 ppm in DMSO-*d*<sub>6</sub>.

Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed by using an UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics) equipped with a 1 kHz smart beam-II laser. The instrument was calibrated before each measurement by using specific molecular weight PS at the molecular weight under consideration. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, > 98%) served as the matrix and was prepared in CHCl<sub>3</sub> at a concentration of 20 mg/mL. The cationizing agent silver trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10:1 (v/v). All samples were dissolved in CHCl<sub>3</sub> at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity. The spectra were recorded in the reflectron mode as well as the linear mode.

Differential scanning calorimetry (DSC) was performed with heating and cooling at a scanning rate of 20 °C/min with a limited temperature range from -80 °C - 300 °C on a Q200 differential

scanning calorimeter (TA Instruments), and the glass transition temperature  $(T_g)$  was measured during the second heating scan.

Thermogravimetric analyses (TGA) were performed on a thermogravimetric analyzer (Discovery TGA, USA) at a heating rate of 10 °C/min from room temperature to 800 °C in a  $N_2$  atmosphere.

Agilent technologies 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (G1946C) with an electrospray source (ESI-MS) was used for classic reversed phase LCMS. Analytic reversed phase HPLC was performed with a Phenomenex Kinetex C18 column (5  $\mu$ , 150 × 4.6 mm) using a solvent gradient (0  $\rightarrow$ 100% acetonitrile in H2O in 15 min) and the eluting compounds were detected through UV-detection ( $\lambda$  = 214 nm). High resolution mass spectrometry (HRMS) was measured with a GCT PremierTM and BRUKER MicroQ-TOF.

## 4. Kinetics of rD-A reactions of *endo-* and *exo-*latent monomers under different temperatures

Temperature plays a vital role in the polymerization as well as the deprotection of stereoisomeric latent monomers. It is envisioned that the *endo*-FMI and the *exo*-FHMI will undergo different deprotection processes. *endo*-FMI (864.8 mg, 5.24 mmol) and *exo*-FHMI (1095.5 mg, 5.24 mmol) were respectively dissolved in DMF (6 mL) in a 20 ml dry reaction vial with a magnetic stir bar. The open vial was stirred at 40 °C, 60 °C and 110 °C. Aliquots were taken intermittently to determine the percent deprotection of furan protecting groups by <sup>1</sup>H NMR spectroscopy using formyl protons of DMF as an internal standard.



Fig. S6 Kinetics of rD-A reactions of endo- and exo- latent monomers

## 5. General Polymerization Procedure for RAFT polymerization of St, *endo*-FMI and *exo*-FHMI with programmable fluctuations of temperature

All polymerization reactions were performed in 50 mL baked Schlenk flasks equipped with a magnetic stir bar and Teflon stopper under argon protection. A small amount of DMF was added to improve the solubility. Take the preparation of St/*endo*-FMI/*exo*-FHMI di-blocky copolymer as an example. The general procedure is as follows. The *endo*-FMI (864.8 mg, 5.24 mmol), *exo*-FHMI (1.0950 g, 5.24 mmol), CPDN (71.2 mg, 0.262 mmol), St (3.0 mL, 26.2 mmol), AIBN (8.6 mg, 0.0522 mmol), ACHN (12.7 mg, 0.0522 mmol) were added into a baked Schlenk flask, and then 3.0

mL DMF was added to improve the solubility. The mixture was then degassed to use by four freezepump-thaw cycles prior and was placed in an oil bath kept at 60 °C subsequently. After predetermined time, the tube was taken out and was removed to in another oil bath pre-stabilized at 110 °C and maintained for predetermined time. In case of the polymer chain losing livingness during the temperature jump, we often add a certain amount of initiator ACHN to the mixture. At predetermined intervals, an aliquot was taken out with a syringe under argon. The polymerization was stopped by opening the flask to the air and quenched to -30 °C. Immediately, the copolymers reaction mixtures were dissolved in DMSO- $d_6$  and determined by <sup>1</sup>H NMR spectroscopy meanwhile were dissolved in DMF containing lithium bromide and analyzed by SEC. The crude copolymer was diluted with THF and precipitated in methanol to obtain the pure product, which was then analyzed by MALDI-TOF mass spectroscopy. Other sequence copolymers were obtained in a similar way.

## **SECTION B. Results and Discussions**

## 1. Control experiment

## **1.1 Characterization of Polystyrene (PS)**

Synthesis of PS by one-shot RAFT polymerization which was conducted at the ratio of  $[St]_0/[CPDN]_0/[ACHN]_0 = 100/20/1/0.2$ ; Temperature sequence: 110 °C (6.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).





**Fig. S7** Synthesis of PS via RAFT polymerization: (a) kinetic plots of St; (b) SEC traces of PS during homopolymerization at 110 °C, the cartoon pattern is not accurate but the illustration is intended to guide the eye. (c) MALDI-TOF mass spectra of PS by using cationization agent of Ag salt and DCTB matrix, the sample was obtained from the homopolymerization of St (2.5 kDa, D = 1.09).

Fig. S8 shows a typical <sup>1</sup>H NMR spectrum recorded during homopolymerization of St. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard.



Fig. S8 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St.  $[St]_0/[CPDN]_0/[ACHN]_0 = 100/1/0.2$ ; Temperature sequence: 110 °C (6.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n = 5.1$  kDa (1.16). Conv.<sub>St</sub> = ( $[I_{5.90-5.75}]_0 - [I_{5.90-5.75}]_0 \times 100\%$ .

## 1.2 Characterization of poly(endo-GB-1)

Synthesis of poly(*endo*-GB-1) by one-shot RAFT binary copolymerization of St/*endo*-FMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[CPDN]_0/[ABVN]_0 = 100/20/1/0.2$ ; Temperature sequence: 40 °C (36.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).



**Fig. S9** (a) SEC curves of poly(*endo*-GB-1) at 40 °C during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide the eye. (b) MALDI-TOF mass spectra of poly(*endo*-GB-1) by using cationization agent of Ag

salt and DCTB matrix. The sample was obtained from the copolymerization of St and *endo*-FMI (1.9 kDa, D = 1.12).

Fig. S10 shows a typical <sup>1</sup>H NMR spectrum recorded during a sequential radical binary copolymerization of St and *endo*-FMI. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard. The conversion of polymerized *endo*-FMI (Conv.*endo*-FMI) was estimated by comparing the integration of 2 protons of remaining *endo*-FMI at 3.49-3.48 ppm ( $I_{3.49-3.48}$ ) and the integration of 2 protons of the released but unpolymerized MI at 6.90-6.87 ppm ( $I_{6.90-6.87}$ ) with the initial undeprotected *endo*-FMI.



Fig. S10 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St and *endo*-FMI. [St]<sub>0</sub>/[*endo*-FMI]<sub>0</sub>/[CPDN]<sub>0</sub>/[ABVN]<sub>0</sub> = 100/20/1/0.2; Temperature sequence: 40 °C (36.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n$  = 4.6 kDa (1.17). Conv.<sub>St</sub> = ([ $I_{5.90-5.75}$ ]<sub>0</sub> - [ $I_{5.90-5.75}$ ]<sub>0</sub> / [ $I_{5.90-5.75}$ ]<sub>0</sub> × 100%; Conv.<sub>endo-FMI</sub> = ([ $I_{3.49-3.46}$ ]<sub>0</sub> - [ $I_{3.49-3.46}$ ]<sub>0</sub> - [ $I_{3.49-3.46}$ ]<sub>0</sub> - [ $I_{3.49-3.46}$ ]<sub>0</sub> × 100%.

## 1.3 Characterization of poly(endo-GB-2)

Synthesis of poly(*endo*-GB-2) by one-shot RAFT binary copolymerization of St/*endo*-FMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[CPDN]_0/[AIBN]_0 = 100/20/1/0.2$ ; Temperature sequence: 60 °C (36.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).

(a) 
$$M_{n, SEC}(\mathcal{D})$$
, Time  
20.4 kDa (1.71), 38 h  
11.2 kDa (1.28), 32 h  
9.3 kDa (1.34), 28 h  
7.7 kDa (1.28), 24 h  
6.7 kDa (1.23), 20 h  
5.8 kDa (1.22), 16 h  
5.1 kDa (1.21), 12 h  
4.3 kDa (1.22), 8 h  
2.8 kDa (1.16), 4 h  
6 7 8 9 10  
Retention time (min)



**Fig. S11** (a) SEC curves of poly(*endo*-GB-2) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide the eye. (b) MALDI-TOF mass spectra of poly(*endo*-GB-2) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St and *endo*-FMI (4.3 kDa, D = 1.22).

### 1.4 Characterization of poly(*exo*-RB)

Synthesis of poly(*exo*-RB) by one-shot RAFT binary copolymerization of St/*exo*-FHMI. The copolymerization was conducted at the ratio of  $[St]_0/[exo-FHMI]_0/[CPDN]_0/[ACHN]_0 = 100/20/1/0.2$ ; Temperature sequence: 110 °C (5.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).



**Fig. S12** (a) SEC curves of poly(*exo*-RB) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide the eye. (b) MALDI-TOF mass spectra of poly(*exo*-RB) by using cationization agent of Ag salt and

DCTB matrix. The sample was obtained from the copolymerization of St and *exo*-FHMI (3.7 kDa, D = 1.16).

Fig. S13 shows a typical <sup>1</sup>H NMR spectrum recorded during a sequential radical binary copolymerization of St and *exo*-FHMI. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard. The conversion of polymerized *exo*-FHMI (Conv.*exo*-FHMI) was estimated by comparing the integration of 2 protons of remaining *exo*-FHMI at 5.15-5.10 ppm ( $I_{5.15-5.10}$ ) and the integration of 2 protons of the released but unpolymerized HMI at 7.02-7.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *exo*-FHMI.



Fig. S13 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St and *exo*-FHMI. [St]<sub>0</sub>/[*exo*-FHMI]<sub>0</sub>/[CPDN]<sub>0</sub>/[ACHN]<sub>0</sub> = 100/20/1/0.2; Temperature sequence: 110 °C (36.0 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n$  = 9.3 kDa (1.28). Conv.<sub>St</sub> = ([ $I_{5.90-5.75}$ ]<sub>0</sub> - [ $I_{5.90-5.75}$ ])/ [ $I_{5.90-5.75}$ ]<sub>0</sub> × 100%; Conv.<sub>*exo*-FHMI</sub> = ([ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> × 100%.

### **1.5** Characterization of poly(*endo/exo*-DT-1)

Synthesis of poly(endo/exo-DT-1) by one-shot RAFT ternary copolymerization of St/endo-

FMI/*exo*-FHMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[CPDN]_0/[AIBN]_0/[ACHN]_0 = 100/20/20/1/0.2/0.2$ ; Temperature sequence: 60 °C (6 h) - 110 °C (3.33 h). St = 3.0 mL, St/DMF = 1/1 (v/v).



(a)  $1^{\text{st}}$  slot, 60 °C,  $M_{\text{n}} = 2.2$  kDa (1.19)

**Fig. S14** MALDI-TOF mass spectra of poly(*endo/exo*-DT-1) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St, *endo*-FMI and *exo*-FHMI (2.2 kDa, D = 1.19).

Fig. S15 shows a typical <sup>1</sup>H NMR spectrum recorded during a sequential radical ternary copolymerization of St/*endo*-FMI/*exo*-FHMI. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard. The conversion of polymerized *exo*-FHMI (Conv.*exo*-FHMI) was estimated by comparing the integration of 2 protons of remaining *exo*-FHMI at 5.15-5.10 ppm ( $I_{5.15-5.10}$ ) and the integration of 2 protons of the released but unpolymerized HMI at 7.02-7.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *exo*-FHMI. The conversion of

polymerized *endo*-FMI (Conv.*endo*-FMI) was estimated by comparing the integration of 2 protons of remaining *endo*-FMI and 4 protons of remaining *exo*-FHMI at 3.50-3.40 ppm ( $I_{3.50-3.40}$ ), the integration of 2 protons of the released but unpolymerized MI at 6.90-6.87 ppm ( $I_{6.90-6.87}$ ), the integration of 2 protons of the released but unpolymerized HMI at 7.02-7.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *endo*-FMI.



Fig. S15 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St/*endo*-FMI/*exo*-FHMI. [St]<sub>0</sub>/[*endo*-FMI]<sub>0</sub>/[*exo*-FHMI]<sub>0</sub>/[CPDN]<sub>0</sub>/[AIBN]<sub>0</sub>/[ACHN]<sub>0</sub> = 100/20/20/1/0.2/0.2; Temperature sequence: 60 °C (6 h) - 110 °C (3.33 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n$  = 4.2 kDa (1.28). Conv.<sub>St</sub> = ([ $I_{5.90-5.75}$ ]<sub>0</sub> - [ $I_{5.90-5.75}$ ])/ [ $I_{5.90-5.75}$ ]<sub>0</sub> × 100%; Conv.<sub>*exo*-FHMI</sub> = ([ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ] - [ $I_{7.02-7.00}$ ]) / [ $I_{5.15-5.10}$ ]<sub>0</sub> × 100%. Conv.<sub>*endo*-FMI = ([ $I_{3.50-3.40}$ ]<sub>0</sub> - 2 × [ $I_{5.15-5.10}$ ] - [ $I_{6.90-6.87}$ ] - [ $I_{7.02-7.00}$ ]) / ([ $I_{3.50-3.40}$ ]<sub>0</sub> - 2 × [ $I_{5.15-5.10}$ ]<sub>0</sub>) × 100%.</sub>

## **1.6** Characterization of poly(*endo/exo*-DT-2)

Sequence-controlled RAFT ternary polymerization of St, *endo*-FMI and *exo*-FHMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[CPDN]_0/[ABVN]_0/[AIBN]_0/[ACHN]_0 = 100/20/20/1/0.2/0.2/0.2;$  Temperature sequence: 40



°C (36 h) - 60 °C (24 h) - 110 °C (1.33 h). St = 3.0 mL, St/DMF = 1/1 (v/v).

**Fig. S16** Synthesis of poly(*endo/exo*-DT-2) by one-shot RAFT ternary copolymerization of St/*endo*-FMI/*exo*-FHMI: (a) kinetic plots; (b) cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) contents of

MI or HMI monomer in polymers as a function of normalized chain length. The model diagram of polymers chains is not accurate but is intended to guide the eye. The  $F_{inst}$  profile has been smoothed.



**Fig. S17** (a) SEC traces of poly(*endo/exo*-DT-2) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide the eye. (b) MALDI-TOF mass spectra of poly(*endo/exo*-DT-2) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St, *endo*-FMI and *exo*-FHMI (4.2 kDa, D = 1.19).

## 1.7 Characterization of poly(*endo/exo-*DT-3)

Sequence-controlled RAFT ternary polymerization of St, *endo*-FMI and *exo*-FHMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[CPDN]_0/[ABVN]_0/[AIBN]_0/[ACHN]_0 = 100/20/20/1/0.2/0.2/0.2;$  Temperature sequence: 60 °C (12 h) - 110 °C (1.25 h) - 40 °C (36 h). St = 3.0 mL, St/DMF = 1/1 (v/v).





**Fig. S18** Synthesis of poly(*endo/exo*-DT-3) by one-shot RAFT ternary copolymerization of St/*endo*-FMI/*exo*-FHMI: (a) kinetic plots; (b) cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) contents of MI or HMI monomer in polymers as a function of normalized chain length. The model diagram of polymers chains is not accurate but is intended to guide the eye. The  $F_{inst}$  profile has been smoothed.



**Fig. S19** (a) SEC traces of poly(*endo/exo*-DT-2) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide

the eye. (b) MALDI-TOF mass spectra of poly(endo/exo-DT-2) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St, *endo*-FMI and *exo*-FHMI (5.6 kDa, D = 1.37).

## 1.8 Characterization of poly(*endo/exo-*DT-4)

Sequence-controlled RAFT ternary polymerization of St, *endo*-FMI and *exo*-FHMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[CPDN]_0/[ABVN]_0/[AIBN]_0/[ACHN]_0 = 100/20/20/1/0.2/0.2/0.2;$  Temperature sequence: 60 °C (12 h) - 40 °C (36 h) - 110 °C (2 h). St = 3.0 mL, St/DMF = 1/1 (v/v).





**Fig. S20** Synthesis of poly(*endo/exo*-DT-4) by one-shot RAFT ternary copolymerization of St/*endo*-FMI/*exo*-FHMI: (a) kinetic plots; (b) cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) contents of MI or HMI monomer in polymers as a function of normalized chain length. The model diagram of polymers chains is not accurate but is intended to guide the eye. The  $F_{inst}$  profile has been smoothed.



**Fig. S21** (a) SEC traces of poly(*endo/exo*-DT-4) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide

the eye. (b) MALDI-TOF mass spectra of poly(*endo/exo*-DT-4) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St, *endo*-FMI and *exo*-FHMI (4.1 kDa, D = 1.34).

## **1.9** Characterization of poly(*endo*-DT)

Sequence-controlled RAFT ternary polymerization of St, *endo*-FMI and PMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[PMI]_0/[CPDN]_0/[ABVN]_0/[AIBN]_0 = 100/20/20/1/0.2/0.2$ ; Temperature sequence: 40 °C (5 h) - 60 °C (17 h). St = 3.0 mL, St/DMF = 1/1 (v/v).



**Fig. S22** Synthesis of poly(*endo*-DT) by one-shot RAFT ternary copolymerization of St/*endo*-FMI/PMI. (a) MALDI-TOF mass spectra of poly(*endo*-DT) by using cationization agent of Ag salt and DCTB matrix. The sample was obtained from the copolymerization of St, *endo*-FMI and PMI (2.1 kDa, D = 1.20).

Fig. S22 shows a typical <sup>1</sup>H NMR spectrum recorded during a sequential radical ternary

copolymerization of St/*endo*-FMI/PMI. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard. The conversion of polymerized *endo*-FMI (Conv.*endo*-FMI) was estimated by comparing the integration of 2 protons of remaining *endo*-FMI at 3.49-3.48 ppm ( $I_{3.49-3.48}$ ) and the integration of 2 protons of the released but unpolymerized MI at 6.90-6.87 ppm ( $I_{6.90-6.87}$ ) with the initial undeprotected *endo*-FMI. The conversion of polymerized PMI at 0.65-0.50 ppm ( $I_{0.65-0.50}$ ) with the initial PMI at 0.85-0.75 ppm ( $I_{0.85-0.75}$ ).



Fig. S23 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St/*endo*-FMI/PMI. [St]<sub>0</sub>/[*endo*-FMI]<sub>0</sub>/[PMI]<sub>0</sub>/[CPDN]<sub>0</sub>/[ABVN]<sub>0</sub>/[AIBN]<sub>0</sub> = 100/20/20/1/0.2/0.2; Temperature sequence: 40 °C (5 h) - 60 °C (17 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n$  = 4.2 kDa (1.28). Conv.<sub>st</sub> = ([ $I_{5.90}$ . 5.75]<sub>0</sub> - [ $I_{5.90-5.75}$ ])/ [ $I_{5.90-5.75}$ ]<sub>0</sub> × 100%; Conv.<sub>*endo*-FMI</sub> = ([ $I_{3.49-3.46}$ ]<sub>0</sub> - [ $I_{3.49-3.46}$ ] - [ $I_{6.90-6.87}$ ]) / [ $I_{3.49-3.46}$ ]<sub>0</sub> × 100%. Conv.<sub>PMI</sub> = [ $I_{0.65-0.50}$ ] / [ $I_{0.85-0.75}$ ]<sub>0</sub> × 100%.

## 1.10 Characterization of poly(endo/exo-TQ)

Sequence-controlled RAFT ternary polymerization of St, endo-FMI, exo-FHMI and PMI.

Synthesis of poly(*endo/exo*-TQ) by one-shot RAFT quaternary copolymerization of St/*endo*-FMI/*exo*-FHMI/PMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[PMI]_0/[CPDN]_0/[ABVN]_0/[AIBN]_0/[ACHN]_0 = 100/20/20/20/1/0.2/0.2/0.2;$  Temperature sequence: 40 °C (4 h) - 60 °C (4 h) - 110 °C (2 h). St = 3.0 mL, St/DMF = 1/1 (v/v).

Fig. S24 shows a typical <sup>1</sup>H NMR spectrum recorded during a sequential radical quaternary copolymerization of St/*endo*-FMI/*exo*-FHMI/PMI. St conversion (Conv.<sub>St</sub>) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90 - 5.75 ppm ( $I_{5.90-5.75}$ ) to the initial integration of St. The region 8.00-7.90 ppm ( $I_{8.00-7.90}$ ), which belonged to the formyl protons of DMF was used as an internal standard. The conversion of polymerized *exo*-FHMI (Conv.*exo*-FHMI) was estimated by comparing the integration of 2 protons of remaining *exo*-FHMI at 5.15-5.10 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *exo*-FHMI. The conversion of polymerized *endo*-FMI (Conv.*endo*-FMI) was estimated by comparing the integration of 2 protons of the released but unpolymerized *endo*-FMI and 4 protons of remaining *exo*-FHMI at 3.49-3.48 ppm ( $I_{3.50-3.40}$ ), the integration of 2 protons of the released but unpolymerized *endo*-FMI and 4 protons of remaining *exo*-FHMI at 5.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *endo*-FMI and 4 protons of remaining *exo*-FHMI at 5.90-6.87 ppm ( $I_{6.90-6.87}$ ), the integration of 2 protons of the released but unpolymerized HMI at 7.02-7.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *endo*-FMI and 4 protons of remaining *exo*-FHMI at 5.90-6.87 ppm ( $I_{6.90-6.87}$ ), the integration of 2 protons of the released but unpolymerized HMI at 7.02-7.00 ppm ( $I_{7.02-7.00}$ ) with the initial undeprotected *endo*-FMI. The conversion of polymerized PMI (Conv.*endo*-FMI) was estimated by Conv.*endo*-6.87 ppm ( $I_{0.65-0.50}$ ) with the initial undeprotected *endo*-FMI. The conversion of polymerized PMI (Conv.*endo*) was estimated by comparing the integration of 3 protons of polymerized PMI at 0.65-0.50 ppm ( $I_{0.65-0.50}$ ) with the initial PMI at 0.85-0.75 ppm ( $I_{0.85-0.75}$ ).



Fig. S24 <sup>1</sup>H NMR spectrum recorded for the RAFT polymerization of St/*endo*-FMI/*exo*-FHMI/PMI. [St]<sub>0</sub>/[*endo*-FMI]<sub>0</sub>/[*exo*-FHMI]<sub>0</sub>/[PMI]<sub>0</sub>/[PMI]<sub>0</sub>/[CPDN]<sub>0</sub>/[ABVN]<sub>0</sub>/[AIBN]<sub>0</sub>/[ACHN]<sub>0</sub> = 100/20/20/20/20/1/0.2/0.2/0.2; Temperature sequence: 40 °C (4 h) - 60 °C (4 h) - 110 °C (2 h). St = 3.0 mL, St/DMF = 1/1 (v/v).  $M_n$  = 9.6 kDa (1.27). Conv.<sub>St</sub> = ([ $I_{5.90-5.75}$ ]<sub>0</sub> - [ $I_{5.90-5.75}$ ]<sub>0</sub> / [ $I_{5.90-5.75}$ ]<sub>0</sub> × 100%; Conv.<sub>*exo*-FHMI = ([ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.00-5.75}$ ]<sub>0</sub> × 100%. Conv.<sub>*endo*-FMI = ([ $I_{3.50-3.40}$ ]<sub>0</sub> - 2 × [ $I_{5.15-5.10}$ ]<sub>0</sub> - [ $I_{5.00-6.87}$ ] - [ $I_{7.02-7.00}$ ]) / ([ $I_{3.50-3.40}$ ]<sub>0</sub> - 2 × [ $I_{5.15-5.10}$ ]<sub>0</sub> × 100%. Conv.<sub>*PMI*</sub> = [ $I_{0.65-0.75}$ ]<sub>0</sub> × 100%.</sub></sub>

### 1.11 Characterization of poly(*endo/exo-DQ*)

Sequence-controlled RAFT ternary polymerization of St, *endo*-FMI, *exo*-FHMI and PMI. Synthesis of poly(*endo/exo*-DQ) by one-shot RAFT quaternary copolymerization of St/*endo*-FMI/*exo*-FHMI/PMI. The copolymerization was conducted at the ratio of  $[St]_0/[endo-FMI]_0/[exo-FHMI]_0/[PMI]_0/[CPDN]_0/ [ACHN]_0 = 100/20/20/20/1/0.2;$  Temperature sequence: 110 °C (4 h). St = 3.0 mL, St/DMF = 1/1 (v/v).



**Fig. S25** Synthesis of poly(*endo/exo-DQ*) by one-shot RAFT ternary copolymerization of St/*endo-FMI/exo-FHMI*: (a) kinetic plots; (b) cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) contents of MI or HMI monomer in polymers as a function of normalized chain length. The model diagram of polymers chains is not accurate but is intended to guide the eye. The  $F_{inst}$  profile has been

smoothed.



**Fig. S26** SEC traces of poly(*endo/exo-DQ*) during the polymerization with bead model of chain sequence distribution. The model diagram of polymers chains is not accurate but is intended to guide the eye.

2. The formulae for normalized chain length,  $F_{cum}$  and  $F_{inst}$ 

# 2.1 The formulae for RAFT binary copolymerization of St and *endo*-FMI/*exo*-FHMI.

Normalized chain length (i) = Conv.<sub>total</sub> (i)/Conv.<sub>max</sub>;

 $Conv_{total} (i) = (20 \times Conv_{endo-FMI or exoFHMI} (i) + 100 \times Conv_{St} (i))/(20 + 100);$ 

Conv.max equals to the maximum value of Conv.total;

 $F_{\text{cum,MI or HMI}}(i) = (20 \times \text{Conv.}_{endo-\text{FMI or exo-FHMI}})/(20 \times \text{Conv.}_{endo-\text{FMI or exo-FHMI}} + 100 \times \text{Conv.}_{\text{st}});$ 

Normalized chain length((i-1) - (i)) = (Conv.<sub>total</sub>  $(i - 1) + Conv._{total} (i)$ )/2Conv.<sub>max</sub>;

 $F_{\text{inst,MI or HMI}}$   $(i - (i - 1)) = 20 \times (\text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i) - \text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i - 1))/[20 \times (\text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i) - \text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i - 1)) + 100 \times (\text{Conv.}_{st}(i) - 1))/[20 \times (\text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i) - 1)]$ 

 $Conv._{St}(i - 1))].$ 

## 2.2 The formulae for RAFT ternary copolymerization of St, *endo*-FMI and *exo*-FHMI.

Normalized chain length (i) =  $Conv_{total}$  (i)/ $Conv_{max}$ ;

Conv.<sub>total</sub> (*i*) =  $(20 \times \text{Conv.}_{endo-FMI} (i) + 20 \times \text{Conv.}_{exo-FHMI} (i) + 100 \times \text{Conv.}_{St} (i))/(20 + 20 + 100);$ 

Conv.max equals to the maximum value of Conv.total;

 $F_{\text{cum,MI or HMI}}(i) = (20 \times \text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i))/(20 \times \text{Conv.}_{endo-\text{FMI}}(i) + 20 \times \text{Conv.}_{exo-FHMI}(i))/(20 \times \text{Conv.}_{endo-\text{FMI}}(i) + 100 \times \text{Conv.}_{st}(i));$ 

Normalized chain length((i-1) - (i)) = (Conv.total (i - 1) + Con v.total (i))/2Conv.max;

 $F_{\text{inst,MI or HMI}}(i - (i - 1)) = 20 \times (\text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i) - \text{Conv.}_{endo-\text{FMI or exo-FHMI}}(i - 1))/[20 \times (\text{Conv.}_{endo-\text{FMI}}(i) - \text{Conv.}_{endo-\text{FMI}}(i - 1)) + 20 \times (\text{Conv.}_{exo-\text{FHMI}}(i) - \text{Conv.}_{exo-\text{FHMI}}(i - 1)) + 100 \times (\text{Conv.}_{\text{St}}(i) - \text{Conv.}_{\text{St}}(i - 1))].$ 

#### 2.3 The formulae for RAFT ternary copolymerization of St, endo-FMI and PMI.

Normalized chain length (i) = Conv.<sub>total</sub> (i)/Conv.<sub>max</sub>;

 $Conv.total (i) = (20 \times Conv.endo-FMI (i) + 20 \times Conv.PMI (i) + 100 \times Conv.st (i))/(20 + 20 + 100);$ 

Conv.max equals to the maximum value of Conv.total;

 $F_{\text{cum,MI or PMI}}(i) = (20 \times \text{Conv.}_{endo-\text{FMI or PMI}}(i))/(20 \times \text{Conv.}_{endo-\text{FMI}}(i) + 20 \times \text{Conv.}_{PMI}(i) + 100 \times \text{Conv.}_{St}(i));$ 

Normalized chain length((i-1) - (i)) = (Conv.total (i - 1) + Conv.total (i))/2Conv.max;

 $F_{\text{inst,MI or PMI}}(i - (i - 1)) = 20 \times (\text{Conv.}_{endo-\text{FMI or PMI}}(i) - \text{Conv.}_{endo-\text{FMI or PMI}}(i - 1))/[20 \times (\text{Conv.}_{endo-\text{FMI}}(i) - \text{Conv.}_{endo-\text{FMI}}(i - 1)) + 20 \times (\text{Conv.}_{PMI}(i) - \text{Conv.}_{PMI}(i - 1)) + 100 \times (\text{Conv.}_{St}(i) - \text{Conv.}_{St}(i - 1))].$ 

## 2.4 The formulae for RAFT quaternary polymerization of St, *endo*-FMI, *exo*-FHMI and PMI.

Normalized chain length (i) = Conv.<sub>total</sub> (i)/Conv.<sub>max</sub>;

 $Conv._{total} (i) = (20 \times Conv._{endo-FMI} (i) + 20 \times Conv._{exo-FHMI} (i) + 20 \times Conv._{PMI} (i) + 100 \times Conv._{PMI} (i) + 100 \times Conv._{endo-FMI} (i) + 100 \times$ 

 $Conv._{st}(i))/(20 + 20 + 20 + 100);$ 

Conv.max equals to the maximum value of Conv.total;

 $F_{\text{cum,MI, HMI or PMI}}(i) = (20 \times \text{Conv.}_{endo-\text{FMI, exo-FHMI or PMI}})/(20 \times \text{Conv.}_{endo-\text{FMI}} + 20 \times \text{Conv.}_{exo-\text{FHMI}} + 20 \times \text{Conv.}_{endo-\text{FMI}} + 100 \times \text{Conv.}_{st});$ 

Normalized chain length((*i*-1) - (*i*)) = (Conv.total (*i* - 1) + Conv.total (*i*))/2Conv.max;

 $F_{\text{inst,MI, HMI or PMI}}(i - (i - 1)) = 20 \times (\text{Conv.}_{endo-\text{FMI, exo-FHMI or PMI}}(i) - \text{Conv.}_{endo-\text{FMI, exo-FHMI or PMI}}(i - 1))$ 

1))/[20 × (Conv.<sub>endo-FMI</sub> (i) - Conv.<sub>endo-FMI</sub> (i - 1)) + 20 × (Conv.<sub>exo-FHMI</sub> (i) - Conv.<sub>exo-FHMI</sub> (i - 1)) + 20

× (Conv.<sub>PMI</sub> (*i*) - Conv.<sub>PMI</sub> (*i* - 1)) + 100 × (Conv.<sub>St</sub> (*i*) - Conv.<sub>St</sub> (*i* - 1))].

3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of the sequence-controlled polymers



Fig. S27 Thermogravimetric analysis curves of St/MIs polymers in a nitrogen stream at the heating rate of 10 °C/min. The onset temperature of decomposition ( $T_{d5}$ ) was determined as the 5% weight loss temperature in thermogravimetric curves.



Fig. S28 Differential scanning calorimetry thermograms of St/MIs polymers at the heating rate of 20 °C/min.

## **SECTION C. Reference**

 X. Gu, L. Zhang, Y. Li, W. Zhang, J. Zhu, Z. Zhang and X. Zhu, *Polym. Chem.*, 2018, 9, 1571-1576.